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CHARACTERISTIC OF MULLITE-ZIRCONIUM CERAMIC OBTAINED FROM POWDERS SYNTHESIZED BY THE HYDROTHERMAL METHOD

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The effect of the hydrothermal method of synthesis of the initial powders using chemical reagents and illite clay as the initial components on the phase composition and structure as well as some properties of mullite-zirconium ceramic was studied. It is shown that mullite and the tetragonal modification of ZrO_2 predominate in the sintered ceramic material but closed pores are also present. As the firing temperature increases and especially with the addition of illite clay the degree of sintering and therefore the compression strength increase. The elastic modulus increases with temperature difference increasing to 1000/20°C, just as with the addition of illite clay, to 35 and 95 GPa, respectively, while with 500/20 it increases to 20 and 22 GPa.

Key words: hydrothermal synthesis, mullite-zirconium ceramic, phase composition, properties.

Mullite and mullite-zirconium ceramic, characterized by elevated high-temperature properties, is capable of operating right up to 1400°C while retaining high mechanical properties [1]. At the present time it is used conventionally as an internal lining in glass- and steel-melting furnaces, in furnaces for firing ceramic materials, in steel-pouring ladles, and so on. This form of ceramic [2, 3] is finding increasingly wider applications in new and simultaneously unconventional technological fields, as an example, as blades, turbines, and nozzles as well as internal coatings of fuel combustion chambers of jet aircraft, where too corrosive a medium (gases from fuel combustion, such as SO_2, SO_3, and so on), which can cause chemical corrosion and, in consequence, degrade the mechanical properties of ceramic material right to destruction, often predominates. Since there is a need to ensure the operation of mullite and mullite-zirconium materials under relatively extreme conditions, the requirements for the mechanical indicators as well as the chemical properties of this ceramic are increasing. Factors such as the form of the initial ceramic powders, the dispersity, activation of ceramic powders, all possible additives, as well as the method of synthesis of the powders, the initial chemical reagents, and other factors can all improve these properties [2 – 4].

There exist many methods [5 – 12] for obtaining and synthesizing mullite and mullite-zirconium ceramic, starting from the conventional techniques for production [5] from the corresponding oxides (or hydroxides) without preliminary

activation of the powders followed by firing of the ceramic material. A number of investigations [6 – 10] present data on the preliminary activation of powders subjected to grinding and simultaneous homogenization for different times — from 4 – 5 h [6 – 8] to 20 – 24 h [9, 10], in some cases even to 30 – 36 h [11], right up to modern methods of synthesis, such as the combustion method [12], the hydrothermal method [2, 3], and so on.

As indicated in [3] the hydrothermal method of synthesizing ceramic powder (at temperatures 270 – 300°C) largely results in the formation of pseudocrystalline forms of aluminosilicate (in all probability, a cluster) with molar ratio of aluminum and silicon oxides 1 : 1. Direct synthesis of stoichiometric mullite with molar ratio of aluminum and silicon oxides 3 : 2 using hydrothermal synthesis is possible at higher temperatures and pressures (starting from 300 to 600 – 700°C at 50 MPa) and with long process time (2 h and longer).

It is indicated in [13 – 15] that this method is most often used to obtain one- and two-component systems (such as ZrO_2, Y_2O_3, Al_2O_3). Studies show [14] that in the case of synthesis of powder of the two-component system $ZrO_2 – Y_2O_3$ to 270°C in 4 h crystal particles 12 – 13 nm in size and weakly aggregated 15 – 20 nm particles are formed.

The objective of the present work is to study the effect of the initial powder synthesized by the hydrothermal method on the development of high-temperature crystalline phases of mullite and ZrO_2 as well as on the degree of sintering and strength properties of ceramic on the basis of the system $Al_2O_2 – SiO_2 – ZrO_2 / Y_2O_3$.

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**TABLE 1.** Components for Synthesis of the Initial Powder

Powder	Component content by weight				
	$Al(NO_3)_3 \cdot 9H_2O$	SiO_2 – aerosol	$ZrO(NO_3)_2 \cdot 2H_2O$	$Y(NO_3)_3 \cdot 6H_2O$	Illite clay
10h	421.75	22.20	10.20	9.95	–
10hi	411.95	21.80	10.00	10.10	8.00

Oxo-salts of the corresponding metals, SiO_2 – aerosol and illite clay, were used as the initial components for the powders (Table 1).

The properties of the chemical reagents used are presented in Table 2.

The initial powder mixtures 10h and 10hi (see Table 1) for hydrothermal synthesis were prepared successively, including the following stages:

– preparation of the water solution

$$Al(NO_3)_3 \cdot 9H_2O + ZrO(NO_3)_2 \cdot 2H_2O + Y(NO_3)_3 \cdot 6H_2O;$$
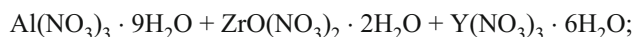
– intense mixing to complete dissolution;

– addition of SiO_2 – aerosil followed by intense mixing with formation of a suspension, pH ~ 1;

– addition of 10% NH_4OH to pH ~ 7, with formation of colloidal "aggregates";

– addition of illite clay to one part of the suspension, intense mixing;

– placement of the prepared suspension into a quartz tube, resistant to high pressures, and securing it inside an autoclave (Fig. 1);

– hydrothermal heating of the initial mixture to about $275 \pm 2°C$ and pressure about $27 – 30$ bar;

– synthesis in an autoclave, duration 4 h.

After hydrothermal synthesis the suspension was dried at $100 – 120°C$, followed by two-stage calcination at $600 – 650$ and $1000°C$ in 30 min.

The powder obtained was subsequently used to prepare the required samples.

The samples for the studies in the form of 10 mm in diameter and 1.5 mm thick disks, 35 mm in diameter and 45 mm high cylinders, and 52 mm long rods with 14×16 mm cross section were obtained from powders by the method of axial pressing under pressure 120 MPa. Firing was conducted in air at temperatures from 1100 to 1500°C.

TABLE 2. Properties of the Chemical Reagents Used for Hydrothermal Synthesis

Chemical reagent	Producer, firm	Content of the main substance, wt.%
$Al(NO_3)_3 \cdot 9H_2O$	Lach/Ner, Czech Republic	98.0
$ZrO(NO_3)_2 \cdot 2H_2O$	ACROS Organics, Belgium	99.9
$Y(NO_3)_3 \cdot 6H_2O$	ACROS Organics, Belgium	99.5
SiO_2 – aerosol	Merck KGaA, Germany	99.0

The rate of heating during firings was 6 K/min with soaking at the maximum temperature for 30 min. The degree of sintering of the samples was evaluated by determining the apparent density, on the basis of the mass-to-volume ratio of the sample and measurement of the open porosity.

The phase composition of the sample was determined by x-ray diffraction (Rigaku model, Japan, with CuK_α radiation with scanning interval $2\theta = 10 – 60°$ and rate 4 K/min) after each firing temperature cycle. The morphology of the particles in the initial powder and the microstructure of the ceramic were determined with a scanning electron microscope (SEM, model JSM-T200, Japan). To determine the particles sizes in the powder after hydrothermal synthesis, just as for the morphology, a SEM and an atomic force microscope (AFM) were used.

Samples in the form of ceramic rods fired at $1400 – 1500°C$ were used to determine the resistance to thermal shock. The resistance of ceramic material to thermal shock was evaluated from the data on the change of the elastic modulus after thermal shock every 200°C in the temperature interval from 500 to 1000°C. The resistance to thermal shock was determined in the following sequence: first the ceramic sample was heated to the chosen temperature (rate of temperature increase 15 K/min with soaking at the maximum temperature for 30 min), after which the samples were removed from the furnace and cooled in air. The elastic modulus was determined after each cycle.

The elastic modulus was determined with the Buzz–o–Sonic testing system (Buzz Mac International, LLC, USA) according to the principle of the measurement of
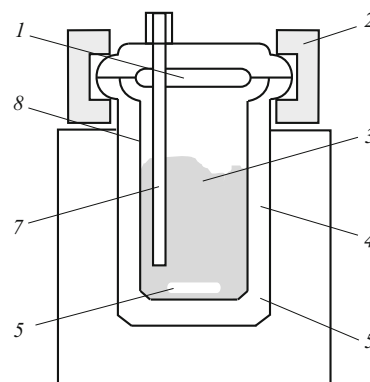
Fig. 1. Schematic image of the autoclave: *1*) rounded filler; *2*) filler for creating pressure; *3*) reaction medium; *4*) shell; *5*) out metal vessel; *6*) heating elements; *7*) thermometer.

shock waves propagating inside a ceramic sample and caught by a special microphone and analyzed with Fourier equipment.

The temperature at which a distortion of the sound caught by the microphone, i.e., for which cracks or other defects appear in the sample, does not yet occur was taken as the quantity characterizing the resistance of the ceramic material to thermal shock.

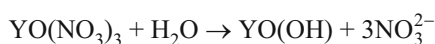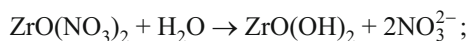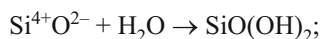The elastic modulus was calculated according to the relation

$$E = 0.9465 \rho f^2 L^4 T_1 / t^2,$$

where E is the elastic modulus, GPa; ρ is the density of the sample, g/cm^3; L is the length of the sample, mm; f is the frequency, Hz; T_1 is the correlation which depends on the dimensions of the experimental sample; and, t is the thickness of the experimental sample, mm.

The compression strength of ceramic samples was determined according to the standard EN 658–2:2003 using TONI Technik Controller TT 0995.

The hydrothermal synthesis process can be conventionally divided into two stages, in each of which the following impossible chemical reactions can occur:
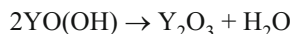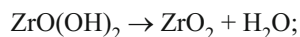
first stage (preparation of the initial suspension):

$$2Al^{3+} + H_2O \rightarrow 2AlO(OH) + NO_3^{2-};$$

$$Si^{4+}O^{2-} + H_2O \rightarrow SiO(OH)_2;$$

$$ZrO(NO_3)_2 + H_2O \rightarrow ZrO(OH)_2 + 2NO_3^{2-};$$

$$YO(NO_3)_3 + H_2O \rightarrow YO(OH) + 3NO_3^{2-}$$

with formation of oxohydroxides

– addition of NH_4OH (pH ~ 7) with formation of colloidal "aggregates" + water;

second stage (hydrothermal synthesis):

$$xAlO(OH) + ySiO(OH)_2 \rightarrow xAl_2O_3 \cdot ySiO_2;$$

$$ZrO(OH)_2 \rightarrow ZrO_2 + H_2O;$$

$$2YO(OH) \rightarrow Y_2O_3 + H_2O$$

with formation of oxides and pseudocrystalline form of alumosilicate (silimanite).

The particles which are formed in the powder after hydrothermal synthesis are largely represented by an amorphous morphology (Figs. 2 and 3). AFM data show that particles in the nanosize range dominate in the powder (Fig. 3).

As the results of the x-ray phase analysis of a ceramic fired at temperatures 1100 – 1400°C show (Fig. 4), the crystallization of the mullite phase and ZrO_2 of the tetragonal modification is already observed at 1200°C. Evidently, nucleation of these phases apparently occurs already at a temperature somewhat below 1200°C. At relatively low temperatures the mullite phase forms as a result of the decomposi-
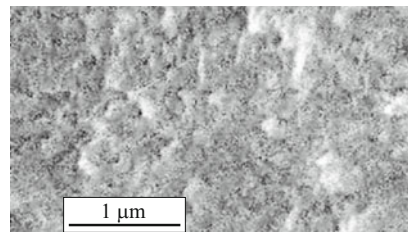

Fig. 2. Photomicrograph obtained with a scanning electron microscope (SEM), particles of hydrothermal ceramic powder, calcined at 600°C.
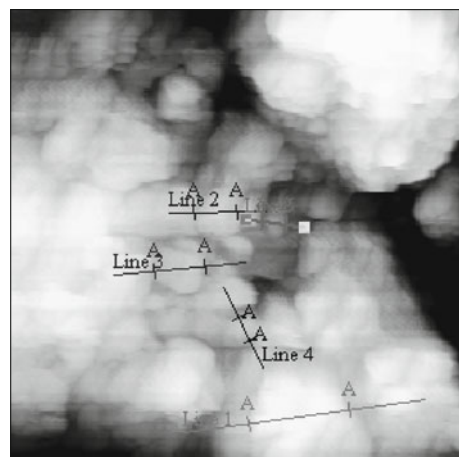

Fig. 3. Photomicrograph obtained in an atomic force microscope (AFM) of a hydrothermal ceramic powder with the addition of illite clay.
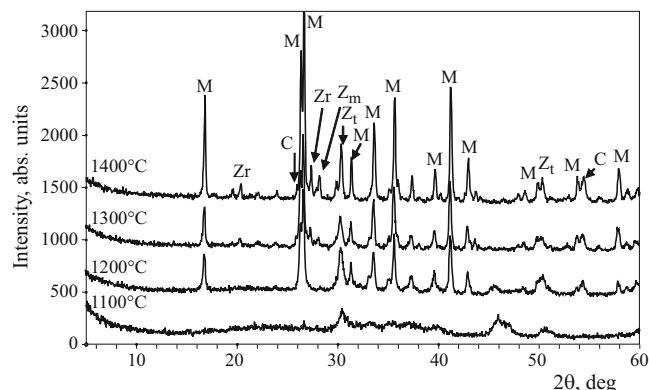

Fig. 4. X-ray phase analysis of ceramic samples from powder with the composition 10h, which were obtained by hydrothermal method and fired at 1100 – 1400°C: M) mullite ($3Al_2O_3 \cdot 2SiO_2$); C) corundum (α-Al_2O_3); Z_t) ZrO_{2tetr}; Z_m) ZrO_{2mon}; Zr) zircon ($ZrSiO_4$).

tion of the pseudocrystalline form alumosilicate (similarly to silimanite), formed in the course of hydrothermal synthesis. The embedding of Y^{3+} ions in the structure of this oxide during the hydrothermal process and subsequent stabilization of tetragonal ZrO_2 during firing promotes the development of
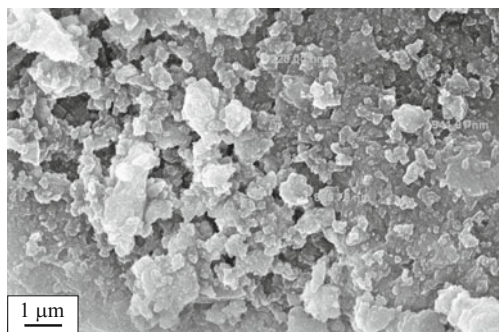
Fig. 5. Photomicrograph (SEM) of the structure of a ceramic sample fired at 1300°C.

Fig. 7. Variation of the elastic modulus of hydrothermal ceramic samples with 10h and 10hi compositions as a function of the thermal shock.
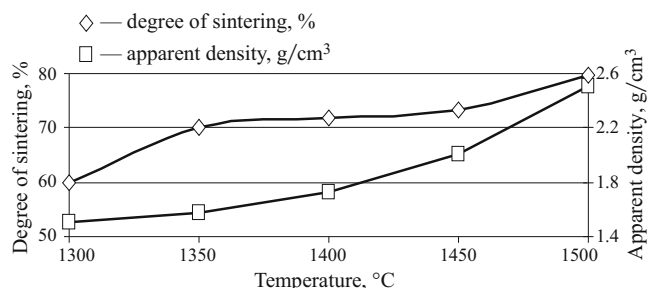

Fig. 6. Variation of the degree of sintering and apparent density of ceramic samples from powder with 10h composition as a function of temperature.

Fig. 8. Comparison of the compression strength of ceramic samples from 10h powder with increasing firing temperature.

ZrO_2 in the tetragonal modification. Higher firing temperatures (1300 – 1400°C) promote further development of the mullite phase and the formation of new crystalline phases — zircon $ZrSiO_4$ and corundum α-Al_2O_3.

The microstructure of the ceramic sample fired at 1300°C (Fig. 5) is represented by the xenomorphic crystalline formations of mullite, and penetrating pores are also present in the sample.

Analysis of the development of sintering and the apparent density with increasing firing temperature (Fig. 6) shows that the sample sinters gradually and therefore the density indicator increases gradually, reaching 80% and 2.55 g/cm³ at firing temperature 1500°C. The very gradual development of these indicators indicates absence of a liquid phase during sintering.

Measurements of the elastic modulus of ceramic samples made from the powders 10h and 10hi (Fig. 7) show that after a thermal shock increased values of the indicators of this quantity are observed with increasing temperature difference with thermal shock and especially for samples containing a clay addition. In all probability, in the presence of a thermal shock, including additional heat treatment of the ceramic sample, not only is the crystal habitus of mullite improved but in addition the crystallization of ZrO_2 in the tetragonal form is more developed [15]. These processes are most intense in the presence of illite clay, which is due to the forma-
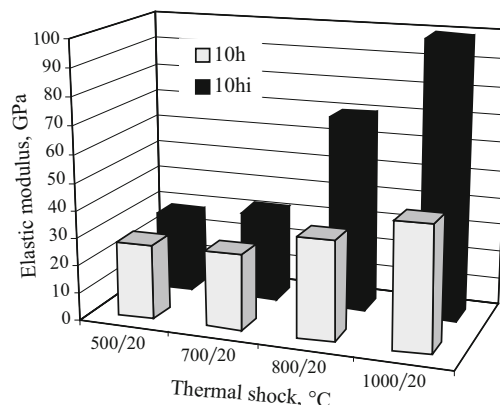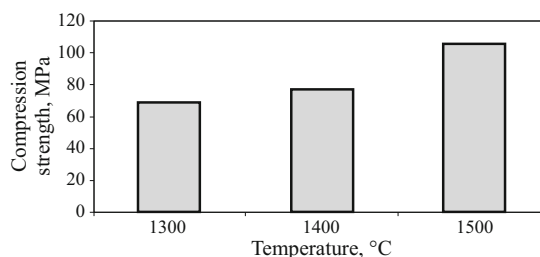
tion of a liquid phase during additional heat treatment at 800 and 1000°C. Judging from the uniform propagation of sound in the samples, including the samples subject to 1000/20°C thermal shock, the samples remain continuous, i.e. heat resistant to temperature ≥ 1000°C.

The compression strength increases uniformly (Fig. 8) with the firing temperature of the samples in the interval 1300 – 1500°C, but they are clearly too low compared with the values for ceramic samples obtained from powders 10 and 24 h after grinding [16]. This difference is mainly due to the low degree of sintering of ceramic from hydrothermal powders. As Fig. 5 shows, the degree of sintering of the samples, for example, at 1400°C is only about 70%, i.e., pore content is very high in fired samples and lowers the strength properties.

In summary, the effect of ceramic powder obtained by hydrothermal synthesis on the development of mullite and tetragonal zirconium phases in the sample of mullite-zirconium ceramic during firing in the temperature range 1100 – 1500°C as well as on the degree of sintering, heat-resistance (elastic modulus), and strength properties were investigated in this work.

It was shown that hydrothermally synthesized initial powder is characterized by an amorphous spherical particle shape with particle size in the nanometer range.

Hydrothermal synthesis promotes the formation of mullite and tetragonal ZrO_2 in ceramic at temperatures $1100 - 1200°C$ and further intense development of these phases with temperature increasing to $1400 - 1500°C$.

Increasing the firing temperature greatly promotes the growth of the apparent density in connection with the formation and development of tetragonal ZrO_2 in a ceramic sample. At the same time samples without illite clay additions are characterized by the presence of closed pores as a result of the absence of a liquid phase during sintering.

It was established that the elastic modulus of ceramic samples is $20 - 100$ GPa and after a thermal shock it tends to increase, more intensely with increasing temperature difference during the thermal shock as well as with the addition of illite clay to the initial powder. The variations of the elastic indicators show that the ceramic samples are heat-resistant to temperatures $\geq 1000°C$.

The compression strength of ceramic samples with no illite clay additions increases monotonically with firing temperature and lies in the range $68.2 - 108$ MPa.

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